The Chlorides

—OF—

Paranitroorthosulphobenzoic Acid.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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ACKNOWLEDGMENT.

This work was suggested by Professor Remsen and was carried out under his direct supervision. To him I desire to express my sincere thanks to the instruction received in the laboratory as well as in the lecture room. I also wish to express my obligations to Professors H. N. Morse and W. B. Clark.

THE CHLORIDES OF PARANITROORTHOSULPHOBENZOIC ACID.

I. Introduction.

In the course of an investigation on the action of aniline upon the chloride of orthosulphobenzoic acid, Remsen and Coates[1] in 1891 obtained two isomeric anilides, with quite different properties, and an anil. This suggested that the chloride was not an individual. In the following year Remsen and Kohler[2] obtained fairly conclusive evidence of the existence of the two chlorides, one of which they obtained as a pure crystalline product, the other as an oil. The crystallized chloride, on treatment with aniline, yielded only two products, the fusible anilide and the anil; the oil yielded besides these two products an infusible anilide. Remsen and Saunders,[3] the next year obtained both chlorides in crystalline form.

In consequence of this work it was deemed advisable to study the action of phosphorus pentachloride upon paranitroorthosulphobenzoic acid in order to see if it would yield isomeric chlorides. The results which I have obtained and which are given in detail in the following pages show that two chlorides are obtained, though Kastle[4] describes only one as the product of such action.

In this article I shall speak of the two chlorides as the symmetrical and the unsymmetrical. The evidence which leads to this view is obtained from the action of ammonia upon the two chlorides. When the unsymmetrical chloride is treated with ammonia it is converted into the ammonium salt of paranitrocyanbenzenesulphonic acid

$$C_6H_3\begin{cases} CN \\ SO_2ONH_4 \\ NO_2 \end{cases}$$

and this compound can be converted into a chloride by treatment with phosphorus pentachloride,

[1] Am. Chem. J., **17**, 311.
[2] Am. Chem. J., **17**, 330.
[3] Am. Chem. J., **17**, 354.
[4] Am. Chem. J., **11**, 180.

$$C_6H_3\begin{cases} CN \\ SO_2Cl \\ NO_2. \end{cases}$$

On the other hand the symmetrical chloride gives with ammonia, the ammonium salt of paranitrobenzoic sulphinide. This ammonium salt

$$C_6H_3\begin{cases} CO \\ SO_2 \\ NO_2 \end{cases} > N.NH_4$$

on treating with acid gives paranitrobenzoic sulphinide.[1]

$$C_6H_3\begin{cases} CO \\ SO_2 \\ NO_2 \end{cases} > NH$$

which crystallizes in fine needles and melts at 209°.

II. Preparation of Material.

100 grams of paranitrotoluene were mixed with 400 grams of fuming sulphuric acid and heated in a balloon flask at a temperature of 100° by being immersed in boiling water. The mixture was kept at this temperature until a portion of it, on being poured into water, goes thoroughly into solution. This heating usually requires from six to eight hours. The mixture is then allowed to cool and poured into cold water. After standing for several hours it is filtered and then neutralized with calcium carbonate. The calcium salt is filtered from the calcium sulphate and converted into the potassium salt by treatment with potassium carbonate. The potassium salt is filtered from the calcium carbonate, and evaporated to crystallization. 100 grams of the potassium salt of paranitrotoluenesulphonic acid, together with 30 grams of potassium hydroxide are dissolved in 5000 cc. of water, the balloon flask containing this solution is immersed in water and heated to a temperature of 100°. When the solution has acquired this temperature 220 grams of potassium permanganate are added, and the mixture heated until the color of the permanganate has entirely disappeared. The amber-colored liquid is then filtered from the manganese hydrate, and the dark-brown

[1] Noyes: Am. Chem. J., 8, 170.

residue thoroughly washed with hot water. The filtrate and washings are then neutralized with hydrochloric acid and evaporated until the neutral potassium salt begins to crystallize out, when a small quantity of the solution is cooled. The whole solution is then allowed to cool and strong hydrochloric acid added in excess when the acid potassium salt of paranitroorthosulphobenzoic acid separates out in beautiful fine white crystals.

III. Action of Phosphorus Pentachloride upon the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid.

When one molecule of the anhydrous acid potassium salt of paranitroorthosulphobenzoic acid is intimately mixed with two molecules of phosphorus pentachloride, no action—or only very slight action—takes place in the cold. 40 grams of the acid potassium salt are mixed with 60 grams of phosphorus pentachloride, and heated in a distilling bulb at a temperature of 150°. The distilling bulb is immersed in a sulphuric-acid bath, and kept at a temperature of 150° for four or five hours. Reaction takes place with the formation of two chlorides,

$$C_6H_3\begin{cases}COOH\\SO_2OK\\NO_2\end{cases} + 2PCl_5 = C_6H_3\begin{cases}CCl_2>O\\SO_2\\NO_2\end{cases} + 2POCl_3 + HCl + KCl.$$

$$C_6H_3\begin{cases}COOH\\SO_2OK\\NO_2\end{cases} + 2PCl_5 = C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 2POCl_3 + HCl + KCl.$$

The yield of the first is from 80 to 90 per cent. and of the second from 10 to 20 per cent. The chlorides must not be heated much above 150°, as decomposition begins at 170°. The yield of the second can be increased to about 30 per cent. by heating in an open dish upon the water-bath. The oily mass is poured into water and washed free from phosphorus oxychloride and potassium chloride. The chlorides are then dissolved in chloroform and the chloroform solution dried by means of calcium chloride. After filtering off the calcium

chloride the solution is allowed to evaporate slowly under a bell-jar free from moist air. From this solution a considerable quantity of the solid (symmetrical) chloride is obtained in crystals which look as if they consisted of monoclinic (?) pinacoids and basal plane. The crystals are filtered off and washed with ice-cold chloroform. After no more crystals can be obtained by this method, more chloroform is added and the solution transferred to an Erlenmeyer flask. This flask is immersed in a freezing-mixture of salt and ice and dry air drawn over the solution for several days. From this more crystals of the symmetrical chloride, mixed with some of the unsymmetrical, are obtained. These are filtered off and washed very quickly with cold chloroform. This dissolves the unsymmetrical chloride with only a very small quantity of the symmetrical chloride. The chloroform solution was evaporated until all the chloroform had been driven off, and the oil was then dissolved in a large volume of petroleum ether (boiling-point 55°–90°). As the ether solution cools it becomes cloudy and then begins to clear up. When this happens, pour the solution into another beaker and allow the solution to cool. From this solution the unsymmetrical chloride then crystallizes almost pure.

This (unsymmetrical) chloride is slightly soluble in petroleum ether, ether 1 part in 200, and from this solvent crystallizes in fine white needles or long flat plates about 3 to 4 mm. broad and 2 to 3 cm. long. They are extremely soluble in ether and chloroform, but crystals cannot be obtained from these solvents. It is decomposed on heating above 160° and melts at 56°–57° (uncorr). This chloride is probably identical with that obtained by Kastle.[1]

The symmetrical chloride can be obtained pure by recrystallizing the first crystals obtained above. It can also be obtained by dissolving the two chlorides in chloroform and shaking this solution with dilute ammonia. The ammonia will act immediately upon the unsymmetrical chloride, and only slightly upon the symmetrical. The chloroform solution is washed with water to free it from ammonia, dried by means of calcium chloride, and allowed to evaporate. From the

[1] Am. Chem. J., 11, 180.

chloroform solution beautiful crystals are obtained as above described. It is soluble also in ether, but less so than the unsymmetrical chloride. It melts at 94–95° (uncorr.) It can be heated in a sealed tube at 150° with phosphorus oxychloride without undergoing any decomposition. Both chlorides when in crystalline form can be left exposed to moist air without undergoing very much decomposition. When the chlorides are first formed—before crystals are obtained—decomposition goes on more readily, judging from the amount of hydrochloric acid given off.

ANALYSES OF THE CHLORIDES.

Portions of both chlorides were heated in a sealed tube with fuming nitric acid. The results obtained were as follow:

0.1933 gram unsym. chloride gave 0.1963 gram AgCl.
0.1933 " " " " 0.1585 " $BaSO_4$.
0.1927 " " " " 0.1950 " AgCl.
0.1927 " " " " 0.1548 " $BaSO_4$.

	Calculated for $C_6H_3\{CO_2, SO_2, NO_2\}>O$	Found. I.	II.
Cl	24.97	25.00	25.02
S	11.25	11.28	11.06

The symmetrical chloride on analysis gave

0.1901 gram sym. chloride gave 0.1935 gram AgCl.
0.1850 " " " " 0.1875 " AgCl.

	Calculated for $C_6H_3\{COCl, SO_2Cl, NO_2\}$	Found. I.	II.
Cl	24.97	25.15	25.06

IV. Action of Water on the Chlorides.

Cold water acts very slowly upon the two chlorides, even after several months the decomposition is incomplete. In hot water they are not readily decomposed, but on boiling the decomposition is complete in a few minutes. The decomposition is about as rapid in one case as in another. With dilute caustic potash they are readily decomposed, and, after cooling,

an excess of hydrochloric acid was added when the characteristic acid potassium salt of paranitroorthosulphobenzoic acid crystallized from each, thus showing that both yield the same decomposition product.

V. Action of Ammonia upon the Chlorides.

Kastle[1] mentions a product of the action of ammonia upon the chloride, but gives no description of it. It was therefore thought best to repeat this work. Five grams of the symmetrical chloride were dissolved in ether and poured into a beaker containing 150 cc. of dilute ammonia. The solution was allowed to stand for several days until the ether had evaporated. From this solution the ammonium salt of paranitrobenzoic sulphinide was obtained. The yield is theoretical. The crystals are rectangular plates or glistening flakes, which do not melt below the boiling-point of sulphuric acid. It is also soluble in alcohol. On adding hydrochloric acid to this salt paranitrobenzoic sulphinide is obtained. The sulphinide[2] crystallizes in fine needles or plates and melts at 209° (uncorr.)

$$C_6H_3\begin{cases}COCl\\SO_2Cl\\NO_2\end{cases} + 4NH_4OH = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4 + 2NH_3Cl + 4H_2O.$$

$$C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4 + HCl = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>NH. + NH_4Cl.$$

When the perfectly dry chloride is dissolved in anhydrous ether and dry ammonia gas passed into the solution the same product is obtained.

0.300 gram of this salt gave 0.05147 gram N.
0.300 " " " " " 0.05178 " N.

Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.NH_4$	Found.	
	I.	II.
N 17.18	17.16	17.26.

[1] Am. Chem. J., 11, 181.

[2] Noyes : Am. Chem. J., 8, 170.

Five grams of the unsymmetrical chloride were dissolved in ether and poured into a beaker containing 100 cc. of dilute ammonia. After the ether had evaporated, nothing crystallized from the solution until it had evaporated to about 50 cc. when a large mass of needles were obtained. These needles grouped themselves in radiating masses or tufts. This product proved to be the ammonium salt of paranitrocyanbenzenesulphonic acid. This salt is also obtained when the mixed chlorides are dissolved in chloroform and shaken with dilute ammonia. From the ammoniacal solution the ammonium salt is obtained on evaporation. From the chloroform solution the symmetrical chloride is obtained.

When ammonia is poured upon the unsymmetrical chloride, solution takes place immediately. In the case of the symmetrical chloride solution is not complete even after twenty-four hours.

$$C_6H_3\begin{cases}CCl_2>O\\SO_2\\NO_2\end{cases} + 4NH_4OH = C_6H_3\begin{cases}CN\\SO_2ONH_4\\NO_2\end{cases} + 2NH_4Cl + 4H_2O.$$

It is probable that an unstable diamide

$$C_6H_3\begin{cases}C(NH_2)_2>O\\SO_2\\NO_2\end{cases}$$

is first formed, and that this by an intra-molecular change passes over into the ammonium salt of paranitrocyanbenzene sulphonic acid.

$$C_6H_3\begin{cases}CN\\SO_2ONH_4\\NO_2\end{cases}$$

The analysis of this salt gave the following results:

0.9965 gram lost over sulphuric acid 0.0687 gram H_2O.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2ONH_4+H_2O.\\NO_2\end{cases}$	Found.
H_2O	6.85	6.90

0.3000 gram of the anhydrous salt gave 0.05148 gram N.
0.3000 " " " " " " 0.05196 " "

	Calculated for $C_6H_3\begin{cases}CN\\SO_2ONH_4\\NO_2\end{cases}$.	Found. I.	II.
N	17.18	17.16	17.32

All nitrogen determinations, which are given in grams, were made by the Kjeldahl method, all others by the absolute method. On adding acid to this salt nothing separated out, even on boiling. As further study was desirable in order to place the formation of this salt beyond doubt, a number of salts derived from these two ammonium salts were made.

VI. Isomeric Salts.

a. The silver salts.

Silver Paranitrocyanbenzenesulphonate, $C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases}+H_2O$.—This salt was prepared by treating ammonium paranitrocyanbenzenesulphonate with silver nitrate. To the hot solution of ammonium paranitrocyanbenzenesulphonate silver nitrate is added and the solution allowed to cool. On cooling the silver salt crystallizes in fine long rectangular needles 2 cm. long. It contains one molecule of water of crystallization which it loses at 100°.

0.6744 gram of this salt lost 0.0354 gram of H_2O at 100°.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OAg+H_2O\\NO_2\end{cases}$.	Found.
H_2O	5.25	5.10

The anhydrous salt on analysis gave the following results:

0.1779 gram gave 0.0760 gram AgCl.
0.1556 " " 0.0667 " "
0.2010 " " 15.1 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases}$.	Found. I.	II.
Ag	32.21	32.16	32.26
N	8.38	8.63	

Silver Salt of the Sulphinide $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.Ag.$ — This

salt was prepared by Noyes[1] by adding silver nitrate to the ammonium salt of the sulphinide. It crystallizes from boiling water (1 part in a 1000) in short fine needles. It is difficultly soluble in boiling water, insoluble in cold. It contains no water of crystallization. It turns brown on exposure to the light.

0.1508 gram gave 0.0645 gram AgCl.
0.1995 " " 0.0856 " "

	Calculated for $C_6H_3\{^{CO}_{SO_2}>N.Ag.$ ^{NO_2}	Found. I.	II.
Ag	32.21	32.20	32.30

b. THE POTASSIUM SALTS.

Potassium Paranitrocyanbenzenesulphonate $C_6H_3\{^{CN}_{SO_2OK+}_{NO_2}$ $1\frac{1}{2}H_2O$.—This salt is prepared by treating the silver salt with sufficient potassium chloride to precipitate all the silver. The solution is filtered from the silver chloride and evaporated to crystallization. The potassium salt crystallizes in beautiful colorless needles 2 to 3 cm. in length and contains $1\frac{1}{2}$ molecules of water of crystallization.

0.3177 gram last 0.0287 gram H_2O at 100°.

	Calculated for $C_6H_3\{^{CN}_{SO_2OK+1\frac{1}{2}H_2O.}_{NO_2}$	Found.
H_2O	9.21	9.03

0.1868 gram anhydrous salt gave 0.0605 gram K_2SO_4.
0.2495 " " " " 0.0802 " "

	Calculated for $C_6H_3\{^{CN}_{SO_2OK.}_{NO_2}$	Found. I.	II.
K	14.66	14.54	14.43

Potassium Salt of the Sulphinide[2] $C_6H_3\{^{CO}_{SO_2}>N.K.$ ^{NO_2}— This salt was prepared by treating paranitrobenzoic sulphinide with potassium carbonate until neutral reaction. It crystallizes in fine leaflets and contains no water of crystallization. It is

[1] Am. Chem. J., 8, 172. [2] Noyes: Am. Chem. J., 8, 170.

easily soluble in hot water, but difficultly soluble in cold.

0.2352 gram of this salt gave 0.0757 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.K.$	Found.
K	14.66	14.45

c. THE BARIUM SALTS.

Barium Paranitrocyanbenzenesulphonate $\left(C_6H_2\begin{cases}CN\\SO_2O\\NO_2\end{cases}\right)_2Ba+2\frac{1}{2}H_2O$.—This salt is made by treating the silver salt with barium chloride. It could not be obtained in well-formed crystals, but formed wart-like masses. It is readily soluble in cold water and contains $2\frac{1}{2}$ molecules of water of crystallization.

0.3747 gram of this salt lost 0.0265 gram H_2O at 100°.

0.3698 " " " " gave 0.1325 " $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CN\\SO_2O\\NO_2\end{cases}\right)_2Ba+2\frac{1}{2}H_2O$.	Found.
H_2O	7.07	7.07
Ba	21.08	21.23

It loses $1\frac{1}{2}$ molecules of water of crystallization over sulphuric acid.

0.2093 gram anhydrous salt gave 0.0822 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CN\\SO_2O\\NO_2\end{cases}\right)_2Ba.$	Found.
Ba	23.17	23.09

Barium Salt of the Sulphinide[1] $\left(C_6H_3\begin{cases}CO\\SO_2>N\\NO_2\end{cases}\right)_2Ba+3H_2O$.—This salt is obtained by treating the sulphinide with barium carbonate. The solution is filtered from the excess of barium carbonate and allowed to crystallize. The salt forms well developed prisms which contain 3 molecules of water of crystallization.

0.3881 gram of this salt lost 0.0329 gram H_2O at 100°.

[1] Noyes: Am. Chem. J., 8, 171.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.\right)_2Ba+3H_2O.$	Found.
H_2O	8.37	8.44

0.3552 gram of the anhydrous salt gave 0.1396 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Ba.$	Found.
Ba	23.17	23.10

d. THE CALCIUM SALTS.

Calcium Paranitrocyanbenzenesulphonate $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ca+7H_2O$.—This salt is formed by treating the silver salt with calcium chloride. It is extremely soluble in water. It is, in fact, soluble in less than its own weight of water. It forms flat plates which are elongated. It loses 3 molecules of water of crystallization over sulphuric acid and 4 more at a temperature of 135.

0.6459 gram lost 0.0543 gram H_2O over sulphuric acid.
0.6459 " " 0.1294 " " at 135°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Ca+7H_2O.$	Found.
$7H_2O$	20.31	20.04

0.2429 gram anhydrous salt gave 0.0661 gram $CaSO_4$.

	Calculated for $C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.)_2Ca$	Found.
Ca	8.09	8.00

Calcium Salt of the Sulphinide $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.\right)_2Ca+6H_2O$.—This salt is formed by treating paranitrobenzoic sulphinide with calcium carbonate. It forms long transparent rectangular columns which soon lose their lustre and become opaque and lose part of their water of crystallization.

0.7069 gram of this salt lost 0.1272 gram water at 100°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\end{matrix}>N.\right)_2Ca+6H_2O.$	Found.
$6H_2O$	17.93	17.99

0.1913 gram anhydrous salt gave 0.0526 gram $CaSO_4$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}>N.\right)_2Ca.$	Found.
Ca	8.09	8.09

e. THE MAGNESIUM SALTS.

Magnesium Paranitrocyanbenzenesulphonate $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Mg + 8H_2O$.—This salt is formed by treating the silver salt with magnesium chloride. It crystallizes in prisms which are somewhat elongated. It is extremely soluble in water and contains 8 molecules of water of crystallization; of these it loses $3\frac{1}{2}$ molecules over sulphuric acid.

0.3800 gram of this salt lost 0.0494 gram H_2O over sulphuric acid.

0.3800 gram of this salt lost 0.0882 gram H_2O at 200°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Mg+8H_2O.$	Found.
$3\frac{1}{2}$ H_2O	13.01	13.00
8 H_2O	23.12	23.21

0.1695 gram of the anhydrous salt gave 0.0411 gram $Mg_2P_2O_7$.

0.2116 gram of the anhydrous salt gave 0.0493 gram $Mg_2P_2O_7$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right)_2Mg.$	Found.	
		I.	II.
Mg	5.09	5.31	5.09

Magnesium Salt of the Sulphinide $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}>N\right)_2Mg + 6\frac{1}{2}H_2O$.—This salt is formed by treating paranitrobenzoic sulphinide with magnesium carbonate. The salt forms beautiful transparent crystals, which seem to be a combination of

orthorhombic (?) domes and prisms. These crystals soon lose their lustre and become opaque. The salt contains $6\frac{1}{2}$ molecules of water of crystallization.

0.2692 gram of this salt lost 0.0527 gram H_2O at 180°.

1.2934 gram of this salt lost 0.2570 gram H_2O at 180°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right.\right)_2Mg+6\frac{1}{2}H_2O$.	Found. I.	II.
$6\frac{1}{2}H_2O$	19.64	19.60	19.87

0.2165 gram of the anhydrous salt gave 0.0523 gram $Mg_2P_2O_7$.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right.\right)_2Mg$.	Found.
Mg	5.09	5.29

f. The Zinc Salts.

Zinc Paranitrocyanbenzenesulphonate $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn+7H_2O$.—This salt is found when the silver salt is treated with zinc chloride. It forms long prismatic columns, is extremely soluble in water, and contains 7 molecules of water of crystallization.

0.7453 gram of this salt lost 0.1477 gram H_2O at 170°.

	Calculated for $\left(C_6H_2\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn+7H_2O$.	Found.
$7H_2O$	19.52	19.82

0.2064 gram anhydrous salt gave 0.0318 gram ZnO.

0.1700 gram anhydrous salt gave 0.0264 gram ZnO.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CN\\SO_2O\\NO_2\end{matrix}\right.\right)_2Zn$.	Found. I.	II.
Zn	12.60	12.38	12.48

Zinc Salt of the Sulphinide $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2>N\\NO_2\end{matrix}\right.\right)_2Zn+4\frac{1}{2}H_2O$.

This salt is formed by treating paranitrobenzoic sulphinide with zinc carbonate. It forms short thick prisms combined

with domes, and resembles very much the corresponding magnesium salt. It contains $4\frac{1}{2}$ molecules of water of crystallization.

0.1861 gram of this salt lost 0.0254 gram H_2O at 125°.

0.4327 gram of this salt lost 0.0593 gram H_2O at 125°.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Zn+4\frac{1}{2}H_2O$.	Found. I.	II.
$4\frac{1}{2}H_2O$	13.49	13.65	13.71

0.2102 gram of the anhydrous salt gave 0.0328 gram ZnO.

	Calculated for $\left(C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N\right)_2Zn$.	Found.
Zn	12.60	12.54

g. The Ethereal Salts.

The Methyl Salt of the Sulphinide $C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.CH_3$.—

This salt is formed by heating the silver salt of paranitrobenzoic sulphinide in a sealed tube at 100° with methyliodide:

$$C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.Ag + CH_3I = C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.CH_3 + AgI.$$

The methyl salt is extracted with boiling alcohol. On cooling the salt crystallizes in leaf-like crystals. It is readily soluble in hot alcohol, but difficultly soluble in cold alcohol. It is also soluble in water. It melts at 179° (uncorr).

0.1575 gram of this salt gave 14.73 cc. N.

0.1561 gram of this salt gave 14.25 cc. N.

	Calculated for $C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.CH_3$.	Found. I.	II.
N	11.59	11.77	11.49

From the product of the action of methyl iodide upon the silver salt of paranitrocyanbenzenesulphonic acid nothing definite has been obtained.

The Ethyl Salt of the Sulphinide $C_6H_3\left\{\begin{matrix}CO\\SO_2\\NO_2\end{matrix}\right.>N.C_2H_5$.—

This salt is formed when the silver salt of the sulphinide is heated in a sealed tube at 100° with ethyl iodide.

$$C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.Ag + C_2H_5I = C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.C_2H_5 + AgI.$$

The mass is extracted with boiling alcohol, filtered, and allowed to cool, when a mass of needles resembling dinitrobenzene is obtained. It is readily soluble in hot alcohol, but difficultly soluble in cold alcohol; it is also soluble in water. It melts at 172° (uncorr).

0.1509 gram of this salt gave 13.53 cc. N.

0.1645 gram of this salt gave 14.68 cc. N.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.C_2H_5$.	Found. I.	Found. II.
N	10.97	11.26	11.21

From the silver salt of paranitrocyanbenzenesulphonic acid I have been unable to obtain an ethereal salt by the action of ethyl iodide, but have obtained a substance which is strongly acid, the nature of which has not yet been determined, but is probably analogous to the orthobenzaminesulphonic acid obtained by Jesurin[1] by the action of alcohol on orthocyanbenzenesulphonic acid.

$$C_6H_3\begin{cases}CN\\SO_2OAg\\NO_2\end{cases} + C_2H_5I = C_6H_3\begin{cases}CN\\SO_2OC_2H_5\\NO_2\end{cases} + AgI.$$

and this then probably reacts thus:

$$C_6H_3\begin{cases}CN\\SO_2OC_2H_5\\NO_2\end{cases} + C_2H_5OH + H_2O = C_6H_3\begin{cases}CONH_2\\SO_2OH\\NO_2\end{cases} + (C_2H_5)_2O.$$

VII. Paranitrocyanbenzenesulphonic Acid.

$C_6H_3\begin{cases}CN\\SO_2OH\\NO_2\end{cases} + H_2O$.—This acid is formed when its silver salt is treated with hydrochloric acid enough to precipitate all the silver. It is also formed by treating the barium salt with sulphuric acid. The acid crystallizes in long prisms

[1] Ber. d. chem. Ges., **26**, 2287.

which contain 1 molecule of water of crystallization. If heated rapidly, it melts between 145° and 150°, but solidifies again immediately. This is due to the fact that the acid goes in solution in its water of crystallization, and when this is driven off it solidifies. It is extremely soluble in water, being soluble in less than its own weight. On being neutralized with potassium carbonate the potassium salt of paranitrocyanbenzenesulphonate is obtained. On heating the acid with caustic potash for some time, ammonia is liberated, and then adding an excess of hydrochloric acid a mass of fine needles resembling the acid potassium salt of paranitroorthosulphobenzoic acid is obtained. When the acid is heated to 130° it loses 1 molecule of water and, if the temperature is then raised to 150°, it begins to increase in weight. This increase is probably due to the oxidation of the cyanogen group. This product is still under investigation.

0.3603 gram of the acid lost 0.0254 gram H_2O at 130°.

0.2503 gram of the acid gave 0.02861 gram N.

0.3033 gram of the acid gave 0.03403 gram N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2OH\\NO_2\end{cases} + H_2O$.	Found. I.	Found. II.
H_2O	7.31	7.06	
N	11.42	11.43	11.23

VIII. Paranitrocyanbenzenesulphone Chloride.

$C_6H_3\begin{cases}CN\\SO_2Cl\\NO_2\end{cases}$.—This chloride is formed when the potassium salt of paranitrocyanbenzenesulphonic acid is treated with phosphorus pentachloride. One molecule of the potassium salt is mixed with 1 molecule of phosphorus pentachloride, and the mixture heated to a temperature of 140° in a sulphuric-acid bath for several hours. The mass is then treated with water to decompose the phosphorus oxychloride and to dissolve the potassium chloride. The chloride is then dissolved in chloroform and dried by means of calcium chloride. The chloroform solution is allowed to evaporate when the chloride crystallizes in long rectangular prisms which

melt at 107°–108° (uncorr). They are soluble in chloroform, ether, and benzene.

0.2640 gram of this chloride gave 0.2538 gram $BaSO_4$.
0.1640 gram of this chloride gave 0.1572 gram $BaSO_4$.
0.2025 gram of this chloride gave 18.75 cc. N.
0.1640 gram of this chloride gave 0.0984 gram AgCl.
0.2640 gram of this chloride gave 0.1544 gram AgCl.
0.1003 gram of this chloride gave 0.0592 gram AgCl.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2Cl.\\NO_2\end{cases}$	Found. I.	II.	III.
Cl	14.38	14.83	14.46	14.59
N	11.40	11.63		
S	13.00	13.23	13.19	

IX. Paranitrocyanbenzenesulphonamide.

$C_6H_3\begin{cases}CN\\SO_2NH_2\\NO_2\end{cases}$.—This amide is formed when paranitrocyanbenzenesulphone chloride is treated with ammonia. 2 grams of the chloride were dissolved in chloroform and added to an aqueous solution of ammonia. The mixture is shaken in a separating-funnel occasionally. The amide separates as an amorphous mass which is filtered off and recrystallized from alcohol. It crystallized in small rectangular blocks resembling cane sugar. It does not melt below 270°. The yield is theoretical.

0.1920 gram of this salt gave 28.02 cc. N.
0.1535 gram of this salt gave 22.79 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2NH_2.\\NO_2\end{cases}$	Found. I.	II.
N	18.33	18.54	18.65

X. Paranitrocyanbenzenesulphonanilide.

$C_6H_3\begin{cases}CN\\SO_2NHC_6H_5\\NO_2\end{cases}$.—This anilide is formed in the same way as the amide. Dissolve 1 gram of the chloride in chloroform; add an aqueous solution of aniline. Heat the solution to

drive off the chloroform. As the chloroform is evaporated the anilide separates as a powder. This powder is recrystallized from alcohol. The yield is theoretical. The anilide crystallizes in fine needles and melts at 207°–208° (uncorr.)

0.1513 gram of this anilide gave 16.97 cc. N.

	Calculated for $C_6H_3\begin{cases}CN\\SO_2NHC_6H_5\\NO_2\end{cases}$.	Found.
N	13.94	14.09

XI. Action of Aniline on the Chlorides of Paranitroorthosulphobenzoic Acid.

a. Action of Aniline on the Unsymmetrical Chloride in the Presence of Water.—The unsymmetrical chloride was added to an excess of aniline in an emulsion of water, 1 gram of the aniline in 30 cc. of water. The mixture was shaken until no more aniline was taken up. The excess of aniline was then distilled off in a current of steam. The liquid was removed by filtration and from the filtrate aniline hydrochloride and the aniline salt of paranitroorthosulphanilidobenzoic acid were obtained. The residue, insoluble in water, was dried and extracted with chloroform. The chloroform on evaporation gave nearly pure fusible anilide of paranitroorthosulphobenzoic acid. The residue from the chloroform extract was dissolved in alcohol and was the infusible anilide. The yield of the infusible anilide was only about 3 per cent., the fusible anilide about 20 per cent., and the aniline salt about 20 per cent.

b. Action of Aniline on the Dry Unsymmetrical Chloride.—One-half gram of the unsymmetrical chloride was gradually mixed with an excess of aniline. The mixture, after being thoroughly ground, was heated on the water-bath for three hours, and then treated as above; there was obtained four-tenths of a gram of the fusible anilide and one-tenth of a gram of the infusible.

c. Action of Aniline upon the Unsymmetrical Chloride in Chloroform Solution.—5 grams of the unsymmetrical chloride were dissolved in chloroform and an excess of aniline added. The mixture was heated to drive off the chloroform and then

heated at 100° for an hour. The mass was then treated as in *a* (above). From the water solution 4 grams of the aniline salt of paranitroorthosulphanilidobenzoic acid and 2.3 grams of the fusible anilide from the chloroform solution were obtained. In another experiment, in which I used the last of the chloride, the chloride was dissolved in chloroform and aniline added in excess. The mixture was kept cold and shaken for a short time. The precipitate which formed in the chloroform solution was filtered and washed with chloroform. It consisted of the infusible anilide and aniline hydrochloride. The chloroform solution was then heated, and from it the fusible anilide mixed with a small quantity of the infusible anilide were obtained.

d. Action of Aniline on the Symmetrical Chloride.—When the symmetrical chloride is treated with an excess of aniline in chloroform, ether or water, the only products are the fusible anilide and aniline hydrochloride. If the chloride is mixed with aniline in the proportion of one molecule of the chloride to one of aniline, the anil is formed; if in the proportion of one molecule of the chloride to two molecules of anitine, the anil is formed together with a very small amount of the fusible anilide; when the proportion is one to four, the fusible anilide is formed.

e. Infusible Anilide.—This is formed best by treating the unsymmetrical chloride dissolved in chloroform with an excess of aniline. The solution must be kept cold, as the yield is diminished by warming. The infusible anilide is precipitated together with aniline hydrochloride, in the chloroform solution. The precipitate is dried, washed with water to dissolve the aniline hydrochloride, and the residue is found to be pure infusible anilide. It is insoluble in water; soluble in alcohol. (Some recent experiments seem to indicate that it undergoes a change by boiling it in alcoholic solution. This is still under investigation.) The product analyzed was the above precipitate insoluble in water. It does not melt on heating to 280°. It dissolves in caustic potash, and differs from the infusible anilide of orthosulphobenzoic acid, in that it is decomposed by it. This substance on analysis gave the following results:

0.1734 gram infusible anilide gave 0.018263 gram N.
0.1818 " " " " 0.019221 " "
0.1925 " " " " 0.1156 " $BaSO_4$.
0.1561 " " " " 0.0907 " "

	Calculated for $C_6H_3\{C(NHC_6H_5)_2>O, SO_2, NO_2$	Found. I.	II.
N	10.58	10.53	10.58
S	8.06	8.25	7.98

It was impossible to get it to crystallize except as wart-like masses.

f. Fusible Anilide.—This is formed in all cases (in part) in which an excess of aniline is used. It is the only product formed when an excess of aniline acts on the symmetrical chloride. In one experiment in which some infusible anilide was boiled in alcohol, it was found to have been changed into the fusible anilide; this is still under investigation. The anilide crystallizes from chloroform in a silky mass. It is soluble in alcohol; insoluble in water; it is dissolved by alkalies and recipitated by acids; by this means it can be obtained free from the anil and the infusible anilide. It melts at 222° (uncorr.) This salt on analysis gave the following results:

0.2455 gram fusible anilide gave 0.5158 gram CO_2.
0.2455 " " " " 0.0874 " H_2O.
0.1502 " " " " 0.0897 " $BaSO_4$.
0.2016 " " " " 17.4 cc. N.
0.2035 " " " " 17.50 " N.

	Calculated for $C_6H_3\{CONHC_6H_5, SO_2NHC_6H_5, NO_2$.	Found. I.	II.	III.
C	57.40	57.34		
H	3.78	3.95		
S	8.06	8.21		
N	10.61		10.84	10.80

g. The Anil. — This is formed when the symmetrical chloride and aniline are heated together in the proportion of one molecule of the chloride to one molecule of aniline. Add the aniline gradually to the chloride and heat the mixture some time in a sulphuric-acid bath. The mass is then ex-

tracted with boiling alcohol. From the alcoholic solution the anil is obtained ; it crystallizes in fine needles ; it is insoluble in alkalies, and by this means it can be separated from the anilides. It melts at 183° (uncorr). On analysis it gave the following results :

0.1562 gram of the anil gave 0.1199 gram $BaSO_4$.
0.1735 " " " " " 0.1314 " "
0.2105 " " " " " 15.82 cc. N.
0.2124 " " " " " 15.67 " "

	Calculated for $C_6H_3\{CO, SO_2, NO_2\}>N.C_6H_5$.	Found. I.	Found. II.
S	10.52	10.55	10.41
N	9.21	9.44	9.27

h. Aniline Salt of Paranitroorthosulphanilidobenzoic Acid.— This is the fourth derivative formed by the action of aniline upon the chloride of paranitroorthosulphobenzoic acid. Its formation is doubtless due to some secondary reactions. It is readily soluble in water from which it crystallizes in fine flakes. On analysis it gave the following results :

0.2664 gram gave 0.5395 gram CO_2 and 0.1029 gram H_2O.
0.2186 " " 0.4414 " " " " 0.0856 " "
0.1428 " " 0.0787 " $BaSO_4$.
0.1434 " " 0.0793 " "
0.2000 " " 16.56 cc. N.
0.2004 " " 16.80 " "

	Calculated for $C_6H_3\{COONH_3C_6H_5, SO_2NHC_6H_5, NO_2\}$	Found. I.	Found. II.	Found. III.	Found. IV.	Found. V.	Found. VI.
C	54.91	55.23	55.05				
H	4.10	4.29	4.35				
N	10.15			10.40	10.55		
S	7.71					7.60	7.58

XII. Action of Paratoluidine on Chlorides.

The symmetrical and the unsymmetrical chlorides were treated in exactly the same way with paratoluidine. On using an excess of paratoluidine the same product was obtained from both chlorides.

a. Paranitroorthosulphobenzotoluide (para)

$C_6H_3\begin{cases}CONHC_6H_4CH_3\\SO_2NHC_6H_4CH_3\\NO_2\end{cases}$.—This is formed by treating either the symmetrical or the unsymmetrical chloride with paratoluidine in chloroform solution or grinding them up together and heating them. It crystallizes from alcohol in fine slightly yellow needles which melt at 234° (uncorr.). It is readily soluble in hot alcohol, difficultly soluble in cold water. It is dissolved by alkalies and reprecipitated by acids. It is found impossible to make any compound analogous to the infusible anilide. On analysis it gave the following results:

0.2497 gram gave 0.5433 gram CO_2 and 0.1019 gram H_2O.
0.2576 " " 0.5617 " " " 0.1077 " "
0.2022 " " 16.46 cc. N.
0.2078 " " 16.97 " "
0.1610 " " 0.0863 gram $BaSO_4$.
0.1805 " " 0.1008 " "

$C_6H_3\begin{cases}CONHC_6H_4CH_3\\SO_2NHC_6H_4CH_3\\NO_2\end{cases}$	Calculated	Found.					
		I.	II.	III.	IV.	V.	VI.
C	59.27	59.34	59.47				
H	4.48	4.54	4.47				
N	9.91			10.23	10.26		
S	7.53					7.37	7.67

b. Paranitroorthosulphobenzotolil (para)

$C_6H_3\begin{cases}CO\\SO_2\\NO_2\end{cases}>N.C_6H_4.CH_3$.—This is formed by treating the symmetrical chloride with paratoluidine in the proportion of one molecule of the chloride to one molecule of the toluidine. The mixture is heated in a sulphuric-acid bath for about one hour. The mass is then extracted with boiling alcohol. On cooling the toluil crystallizes from the alcohol in fine needles which melt at 164–165° (uncorr.). It is soluble in hot alcohol, insoluble in water and alkalies. It can be purified by dissolving the product in alkalies as in the case of the anil. On analysis it gave the following results:

0.1042 gram substance gave 0.0761 gram $BaSO_4$.
0.1061 " " " 0.0786 " "
0.1062 " " " 7.55 cc. N.
0.1065 " " " 7.62 " "

	Calculated for $C_6H_3\begin{cases} CO \\ SO_2 \\ NO_2 \end{cases}>N.C_6H_4CH_3$.	Found. I.	Found. II.
S	10.06	10.04	10.19
N	8.83	8.93	8.99

Conclusion.

Several conclusions seem to be justified by the results of the experiments described in this paper:

1. When phosphorus pentachloride acts upon paranitro-orthosulphobenzoic acid two isomeric chlorides are formed, one of which has the formula $C_6H_3\begin{cases} CCl_2 \\ SO_2 \\ NO_2 \end{cases}>O$ and melts at 56°–57° (uncorr); the other has the formula $C_6H_3\begin{cases} COCl \\ SO_2Cl \\ NO_2 \end{cases}$ and melts at 94°–95° (uncorr.).

2. When the two chlorides are treated with ammonia the first or unsymmetrical, gives the ammonium salt of paranitrocyanbenzenesulphonic acid; the other gives the ammonium salt of paranitrobenzoic sulphinide.

3. When the silver salts are treated with hydrochloric acid, the silver salt of paranitrocyanbenzenesulphonic acid gives the free paranitrocyanbenzenesulphonic acid, while the silver salt of the sulphinide gives paranitrobenzoic sulphinide.

4. When the silver salts are treated with methyl and ethyl iodide, the silver salt of paranitrobenzoic sulphinide yields ethereal salts of the sulphinide, while the silver salt of paranitrocyanbenzenesulphonic acid yields a product which is strongly acid. The nature of this product has not yet been determined.

5. When the two chlorides are treated with aniline the symmetrical chloride yields an anil and a fusible anilide, while the unsymmetrical chloride yields an infusible anilide which seems to be easily decomposed. It also yields the fusible anilide.

6. With paratoluidine both chlorides yield the same toluide.

BIOGRAPHICAL.

George William Gray, the author of this dissertation, was born at Cumberland, Md., on August 12th, 1867. He was educated in the public schools of Maryland and Washington, D. C. He entered Johns Hopkins University in 1887, and graduated from there in 1890, having pursued the chemical-physical course. From 1890–1892 he was with the Baltimore Sugar Refinery and the Maryland Steel Company as chemist. He returned to Johns Hopkins University in the fall of 1892, and since that time has pursued advanced courses in chemistry.